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MANUFACTURE OF NITROGENOUS CELLULOSE DERIVATIVES

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Our present invention relates to the manufacture of cellulose.

One of its objects is to provide a process of manufacturing nitrogenous cellulose derivatives. Another object are the nitrogenous cellulose derivatives. Further objects will be seen from the detailed specification following hereafter.

We have found that nitrogenous compounds of cellulose are easily obtained by reacting on cellulose with ethylene-imine. The ethylene-imine may be brought to reaction on cellulose at a raised temperature in gaseous form; this may be easily realized in view of the low boiling point of the ethylene-imine. The ethylene-imine may also be brought into reaction with the cellulosic material while dissolved in a suitable solvent which does not react with the ethylene-imine. Such solvents are, for instance, water, or organic solvents, for instance, toluene, xylene, benzene or highly boiling benzene, that is to say aromatic and aliphatic hydrocarbons. The process according to this invention is of particular importance for the treatment of cellulosic fibers which are intended to be dyed by acid wool dyes, because the treated fibers must not be pretreated with a lye or the like before dyeing. If the treatment of the cellulosic material is not performed in an aqueous solution the cellulosic material is preferably used in air dry condition. The cellulosic material may also be used while having a lesser content of moisture, however, in this case the speed of the reaction is decreased. The interaction occurs at temperatures from room temperature up to 120° C., the range from 80 to 100° C. being preferred. After the treatment with ethylene-imine the fibers are washed with an acid solution and then with water. At a higher temperature a greater amount of nitrogen is introduced into the cellulosic material, and the remaining conditions being the same a higher content of nitrogen is taken up by the fibers if the cellulosic material contains more moisture.

When treating the cellulosic material with gaseous ethylene-imine there is obtained a more uniform product when circulating the current of gas and changing periodically the direction of the current.

If the cellulosic material is to receive a higher content of nitrogen the treatment with imine is repeated several times, whereupon the fibers are thoroughly washed with hot water. In this manner there may be reached a content of nitrogen of 10% and more.

The following examples illustrate the invention:

Example 1.—55 grams of air-dry viscose staple fiber which have been subjected to a vacuum in an autoclave are heated at 100° C. in the latter with 10 cc. of ethylene-imine vapour for 4 hours. After this time has elapsed the ethylene-imine has completely disappeared. The fiber is washed with water, with dilute sulfuric acid and again with water. It is feebly yellow, contains 2.45 percent. of nitrogen and is dyed very strongly by acid wool-dyestuffs.

Example 2.—55 grams of dry viscose staple fiber are heated at 100° C. as described in Example 1, with 10 cc. of ethylene-imine for 5½ hours. The product, treated as described in Example 1, contains 1.63 per cent. of nitrogen.

Example 3.—55 grams of air-dry viscose staple fiber (8 per cent H₂O) are in a vacuum treated for 23 hours as described in the preceding examples, with 10 cc. of ethylene-imine, at 70° C. The product contains 1.73 per cent of nitrogen.

Example 4.—100 grams of artificial silk cut into staples are pressed into a solution of 10 cc. of ethylene-imine in 90 cc. of water and heated while sealed for about 2 hours to 100° C. The washed product contains 1.44% of nitrogen.

Example 5.—250 grams of artificial silk cut into staples are introduced into a solution of 50 cc. of ethylene-imine in 5 liters of toluene and heated to 80° C. while repeatedly shaking. Hereafter the toluene is removed by suction and the fibers washed with methanol and water and dried. The fibers contain 2.07% of nitrogen.

Example 6.—In a cylindrical vessel of 10 liters capacity there are introduced 5 kilos of artificial silk from viscose tightly packed between two sieves. The lids of the vessel in front of the sieves are provided with an inlet and an outlet tube. After the fibers have been introduced the vessel is closed and the inlet and outlet tube are connected with a pump for the production of a gas circulation of about 90 liters per minute. The whole apparatus is then heated to 80° C., and then there are introduced into the gas circulation 1200 cc. of ethylene-imine in the course of half an hour. The ethylene-imine becomes immediately gaseous at the temperature of the apparatus and is pressed in this condition through the fibers. The direction for the current of gas is periodically reversed after 5 minutes. After washing with hot water the fibers have a content of nitrogen of 2.12%.

Example 7.—100 grams of artificial silk made

from linters are pressed into a solution of 20 cc. of ethylene-imine dissolved in 80 cc. of water in a pressure vessel and heated to 100° C. for 2 hours. The fibers are washed and a-new treated with imine in the same manner. This operation is performed 7 times with the difference that the last two times there are applied only 10 cc. of imine. The fibers have the following content of nitrogen after the single operations:

	Percent N
1. Treatment	0.84
2. Treatment	1.97
3. Treatment	3.57
4. Treatment	5.34
5. Treatment	8.11
6. Treatment	8.83
7. Treatment	9.48

When heating a cellulosic material treated according to this invention and containing at least 1% of nitrogen with a 2 per cent solution of furfural to 100° C. the material assumes a dark brown color. Nitrogen containing cellulosic materials made according to other processes remain uncolored or assume only a yellow color when treated in the manner.

What we claim is:

1. A process of introducing nitrogen into cellulose according to which cellulose is subjected to the action of ethylene-imine.
2. A process of introducing nitrogen into cellulose according to which cellulose is subjected to the action of ethylene-imine in gaseous condition.
3. A process of introducing nitrogen into cellulose according to which cellulose is subjected to

the action of ethylene-imine dissolved in a solvent which does not react with ethylene-imine.

4. A process of introducing nitrogen into cellulose according to which cellulose is subjected to the action of ethylene-imine at a temperature between 80 to 100° C.

5. A process of producing cellulose derivatives containing nitrogen which comprises introducing artificial silk from viscose cut in staples tightly packed into a vessel, heating said vessel to 80° C. and circulating a current of gaseous ethylene-imine at a temperature of 80° C. through said fibers.

6. A process of producing cellulose derivatives containing nitrogen which comprises introducing artificial silk from viscose cut in staples tightly packed into a vessel, heating said vessel to 80° C. and circulating a current of gaseous ethylene-imine at a temperature of 80° C. through said fibers while changing the direction of the current of gas periodically.

7. A process of producing cellulose derivatives containing nitrogen which comprises heating artificial silk made from linters with a solution of 20 cc. of ethylene-imine in 80 cc. of water in a sealed vessel to 100° C., washing the resulting product, and repeating this operation several times.

8. A process of producing cellulose derivatives containing nitrogen which comprises heating artificial silk from viscose cut in staples with ethylene-imine to 100° C. in a pressure vessel, washing the resulting product with water, then with dilute sulfuric acid, and again with water.

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